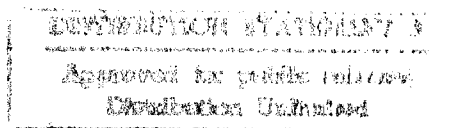


Chlorophenylalkyl-Substituted Carboxylic Acids and Silanes Designed as Adhesion Promoters

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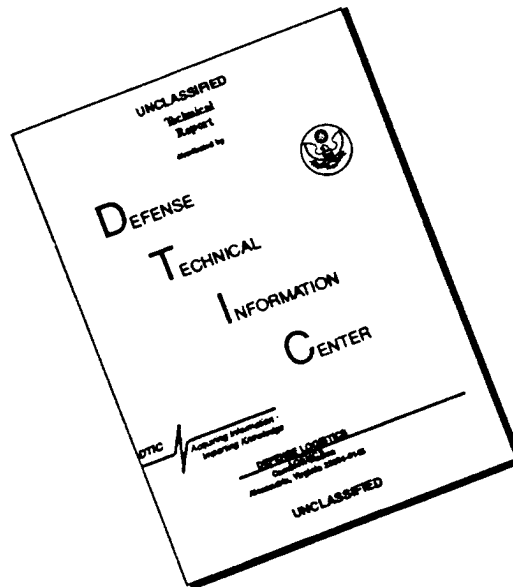


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ABSTRACT

The six new carboxylic acids of this study feature a terminal p-chlorophenyl substituent, a polymethylene spacer, and either one or two carboxyl groups. The carboxyl groups may be replaced by $-\text{SiCl}_3$ or $-\text{Si}(\text{OC}_2\text{H}_5)_3$ groups. Such structures are designed to promote adhesion between a solid substrate and an organic resin by forming a monolayer strongly attached to the substrate and exposing a chlorophenyl outer surface which is easily wet by the resin. Multistep syntheses were carried out for the preparation of monocarboxylic acids $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{n-1}\text{CO}_2\text{H}$, where n is 12, 14, 18, and 20, via Friedel-Crafts reactions and Wolff-Kishner reductions. Some also used a subsequent LiAlH_4 reduction. Succinic and glutaric acids substituted in the alpha position by a $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{12}$ -substituent were prepared through malonic ester syntheses. The acids were characterized by melting points, neutralization equivalents, and elemental assays. NMR spectra showed that the chlorine substitution is at least 95% para. Gas-liquid chromatography was used to assess the purity of both intermediates and products; most of the acids had purities exceeding 97.5%. Principal impurities were the unchlorinated analogs and lower homologs. The Friedel-Crafts method was employed to prepare $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_2\text{SiCl}_3$; this compound and its trimethoxy and triethoxy analogs were characterized by conventional criteria.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C02-17
Project RR 007-08-44-5502

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CHLOROPHENYLALKYL-SUBSTITUTED CARBOXYLIC ACIDS AND SILANES DESIGNED AS ADHESION PROMOTORS

INTRODUCTION

Most commercial finishes for glass fiber form surfaces which are not readily wet by the resins used for glass fiber impregnation. To correct this deficiency in adhesion, redesign of existing coupling agents or adhesion promoters has been proposed (1). The new concept (Fig. 1) utilizes monolayers of appropriate design for promoting adhesion between an organic resin and a solid substrate. The new structures reported here feature a terminal chlorophenyl substituent exposing an outer surface which is readily wet by resins, a polymethylene spacer allowing outward orientation of the exposed group, and at the opposite end a reactive group capable of chemically bonding to the solid substrate. More than one reactive group in the molecule may be desirable; for example we have investigated the use of one or more carboxyl groups. In the case of two terminal carboxyl groups they should be separated by more than one carbon atom to avoid sensitivity to decarboxylation. Alternatively the single carboxyl group may be replaced with $-\text{SiCl}_3$, $-\text{Si}(\text{OEt})_3$, or other groups.

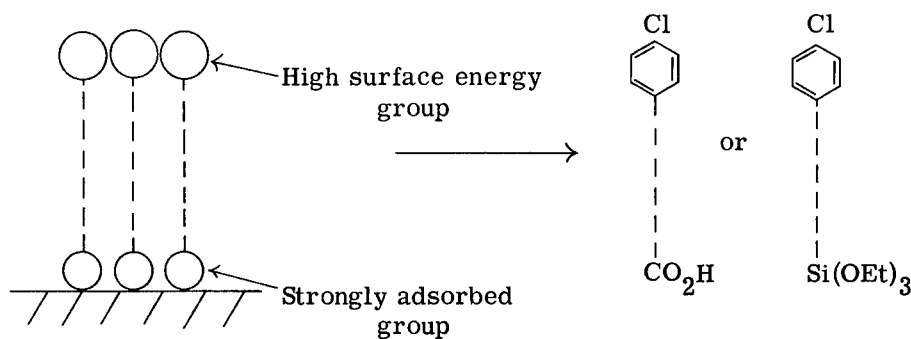


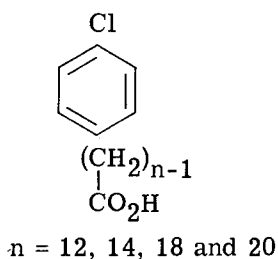
Fig. 1 - Structural concept for adhesion promoters

The present study outlines methods for preparing four new monocarboxylic acids, two new dicarboxylic acids, together with one known and two new substituted silanes. All comply with the above structural concepts. Structures of the six acids are given in Fig. 2.

All six of the chlorophenyl-substituted carboxylic acids are derived from acid chlorides of long-chain aliphatic half esters. To prepare these uncommon intermediates in sufficient amounts, practicable preparative methods had to be developed. Methods are given for converting appropriate α, ω -dicarboxylic acids to the corresponding acid chloride half esters.

Certain of the p-chlorophenyl-substituted carboxylic acids are related products in a multistep synthesis. A schematic outline of synthetic procedures is presented to clarify these relationships. Properties of seven new p-chlorophenyl-substituted intermediates and six new p-chlorophenyl-substituted carboxylic acids are reported. All of the thirteen

Monocarboxylic acids



Dicarboxylic acids

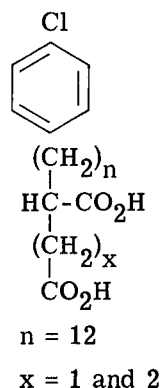


Fig. 2 - The structures of six chlorophenyl-substituted carboxylic acids

new compounds have been characterized by conventional criteria. Both gas-liquid chromatography and nuclear magnetic resonance are used to assess the purity of the carboxylic acids and their intermediates.

SYNTHETIC METHODS

 α,ω -Dicarboxylic Acids: Dodecanedioic and Octadecanedioic Acid

The dodecanedioic acid, m.p. 125 to 127°C, was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. Hünig's 1.6-g preparative procedure for octadecanedioic acid (2) was scaled up for 90-g batches in accordance with his large-scale method for docosanedioic acid (3). The modified procedure involves initial reactions between 1-morpholino-1-cyclopentene and suberyl chloride leading to 2,2'-suberyldicyclopentanone. The latter reacts with alcoholic sodium hydroxide to yield disodium 6,13-diketooctadecanedioate. Wolff-Kishner reduction of the salt of the diketo acid followed by recrystallization from methyl ethyl ketone gives fairly pure octadecanedioic acid (m.p. 121 to 124°C; 57% yield; 96% purity). The principal impurity is tridecanedioic acid.

Diesters: Diethyl Dodecanedioate and Diethyl Octadecanedioate

Both diesters were prepared by the method reported for diethyl adipate (4). The diethyl dodecanedioate (b.p. 165°C/1.3 mm; n_D^{20} 1.4396; m.p. 16°C; 99.4% purity by gas-liquid chromatography) is obtained in 97% yield by distillation. The diethyl octadecanedioate (m.p. 47 to 48°C, 99.0% purity by gas-liquid chromatography) is furnished in 56% yield by recrystallizing the undistilled diester (prepared from the 96% diacid) from ethyl alcohol (e.g., 1 g of diester per 4 g of alcohol). Physical properties observed for the respective diesters agree with reported values (5-7).

Half Esters: Ethyl Hydrogen Dodecanedioate and Ethyl Hydrogen Octadecanedioate

Practicable methods had to be developed for converting the diethyl esters to the respective half esters in batches as large as 100 g. The improved process gives a relatively

high conversion of the reacted diester to the half ester and allows a quantitative recovery of the unreacted diester which can be submitted to another batch operation.

Alcoholic sodium hydroxide solution (26 ml of 1N) is added dropwise during 30 min to a stirred mixture of diethyl dodecanedioate (15.0 g; 0.0524 mole) and ethyl alcohol (30 ml). Water (60 ml) is added and stirring is continued (ca. 15 min) until the pH reaches 8.0. Extraction of the aqueous mixture with petroleum ether (30 to 60°C boiling range; 2 x 120 ml) removes unreacted diethyl dodecanedioate (8.60 g; 0.0300 mole). Acidification of the aqueous layer with 600 ml of 0.1N hydrochloric acid precipitates ethyl hydrogen dodecanedioate and dodecanedioic acid. Both acids are extracted with ether (2 x 150 ml). After drying and concentrating the extract the residue is melted by warming to 60°C, poured into 250 ml of petroleum ether, and allowed to stand 1 hour at 25°C for equilibration. Precipitated dodecanedioic acid is removed by filtration (1.80 g; 0.0078 mole). The filtrate is cooled to -10°C and filtered to collect the ethyl hydrogen dodecanedioate (3.72 g; 0.0144 mole; m.p. 49 to 50°C in agreement with the reported value (8)). The yields based upon the amount of diester consumed are 64.3% half ester and 34.8% diacid, a total of 99.1%. Yields based upon the diester used are 27.5% half ester, 14.9% diacid, and 57.3% recovered diester, a total of 99.7%.

Diethyl octadecanedioate can be prepared by the same stoichiometry, provided the diester is dissolved in 4 times as much alcohol (4 x 30 ml), the saponification step is performed at 60°C, and the final mixture of diacid and half ester is resolved in hexane. The modified procedure yields ethyl hydrogen octadecanedioate melting at 71.5 to 72.5°C in agreement with the literature value (7). Yields based upon the amount of diester consumed are 90.0% half ester and 3.3% diacid. Based upon the amount of diester used they are 44.4% half ester, 1.6% diacid, and 51.0% recovered diester.

Acid Chlorides of Half Esters

The half esters are converted to the corresponding half ester acid chloride by allowing each to stand overnight with two equivalents of thionyl chloride. Unreacted thionyl chloride is removed at reduced pressure, the last traces being removed by redistillation with 50-ml portions of benzene. The residual acid chlorides are used for the preparation of the keto esters.

Keto Esters: ω -(p-Chlorobenzoyl)alkanoic Acid Esters

The intermediate keto esters $p\text{-ClC}_6\text{H}_4\text{CO}(\text{CH}_2)_{10}\text{CO}_2\text{Et}$ and $p\text{-ClC}_6\text{H}_4\text{CO}(\text{CH}_2)_{17}\text{CO}_2\text{Et}$ were synthesized from α,ω -dicarboxylic acids via the major steps shown in Fig. 3. Acid

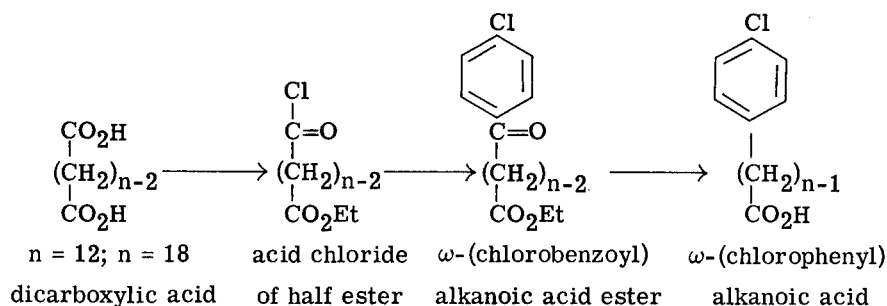


Fig. 3 - Scheme for the synthesis of the keto esters $p\text{-ClC}_6\text{H}_4\text{CO}(\text{CH}_2)_{10}\text{CO}_2\text{Et}$ and $p\text{-ClC}_6\text{H}_4\text{CO}(\text{CH}_2)_{17}\text{CO}_2\text{Et}$ from α,ω -dicarboxylic acids

Table 1
Analysis and Properties of Intermediates

No.	Compound	Formula	Properties				Analyses (%)					
			B.P. (°C/ mm Hg)	M.P. (°C)	N.E.		C		H		Cl	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1	p-ClC ₆ H ₄ CO(CH ₂) ₁₀ CO ₂ H	C ₁₈ H ₂₅ ClO ₃	—	105-107	324.9	324.0	66.55	66.56	7.66	7.66	10.91	10.86
2	p-ClC ₆ H ₄ CO(CH ₂) ₁₆ CO ₂ H	C ₂₄ H ₃₇ ClO ₃	—	110-112	409.0	409.9	70.48	70.53	9.12	9.21	8.67	8.83
3	p-ClC ₆ H ₄ (CH ₂) ₁₂ OH	C ₁₈ H ₂₉ ClO	199/1.0	32-34	—	—	72.82	72.83	9.85	10.02	11.94	11.95
4	p-ClC ₆ H ₄ (CH ₂) ₁₈ OH	C ₂₄ H ₄₁ ClO	—	58-60	—	—	75.65	76.05	10.86	10.98	9.31	8.90
5	p-ClC ₆ H ₄ (CH ₂) ₁₂ Br	C ₁₈ H ₂₈ BrCl	210/1.0	—	—	—	60.09	59.55	7.85	7.80	9.85 (22.21)*	9.85 (21.17)*
6	p-ClC ₆ H ₄ (CH ₂) ₁₈ Br	C ₂₄ H ₄₀ BrCl	—	44-46	—	—	64.93	64.50	9.08	9.02	7.99 (18.00)*	8.46 (18.85)*
7	p-ClC ₆ H ₄ (CH ₂) ₁₂ CH(CO ₂ Et)CO ₂ Et	C ₂₅ H ₃₉ ClO ₄	245/1.5	—	—	—	68.39	68.49	8.95	8.90	8.08	8.00

*Bromine assays.

Table 2
Analysis and Properties of Carboxylic Acids

No.	Compound	Formula	Properties			Analyses (%)					
			M.P. (°C)	N.E.		C		H		Cl	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
8	p-ClC ₆ H ₄ (CH ₂) ₁₁ CO ₂ H	C ₁₈ H ₂₇ ClO ₂	67-68	310.9	313.0	69.55	69.68	8.75	8.80	11.41	11.65
9	p-ClC ₆ H ₄ (CH ₂) ₁₃ CO ₂ H	C ₂₀ H ₃₁ ClO ₂	70-70.5	337.4	338.9	70.88	70.65	9.22	9.31	10.46	10.37
10	p-ClC ₆ H ₄ (CH ₂) ₁₇ CO ₂ H	C ₂₄ H ₃₉ ClO ₂	74-75	395.0	396.0	72.97	73.26	9.95	10.26	8.98	8.61
11	p-ClC ₆ H ₄ (CH ₂) ₁₉ CO ₂ H	C ₂₆ H ₄₃ ClO ₂	78-79	423.1	424.0	73.81	73.83	10.24	10.31	8.38	8.31
12	p-ClC ₆ H ₄ (CH ₂) ₁₂ CH(CO ₂ H)CH ₂ CO ₂ H	C ₂₂ H ₃₃ ClO ₄	87-88	198.5	198.9	66.57	66.60	8.38	8.40	8.93	8.88
13	p-ClC ₆ H ₄ (CH ₂) ₁₂ CH(CO ₂ H)CH ₂ CH ₂ CO ₂ H	C ₂₃ H ₃₅ ClO ₄	85-86	205.5	206.7	67.22	67.52	8.58	8.63	8.63	8.56

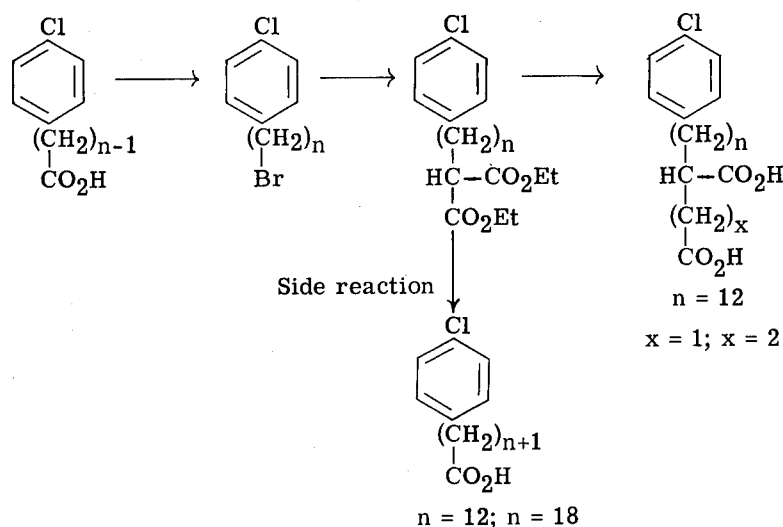


Fig. 4 - Scheme for the synthesis of $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{13}\text{CO}_2\text{H}$ and $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{19}\text{CO}_2\text{H}$ from monoalkylated malonic esters

Dicarboxylic Acids: ω -(p-Chlorophenyl)dodecylsuccinic Acid and 2-[ω -(p-Chlorophenyl)dodecyl]glutaric Acid

Figure 4 outlines major steps in the synthesis of the two dicarboxylic acids. The final step requires alkylation of the diethyl ω -(p-chlorophenyl)dodecylmalonate by modifications of the method given in Ref. 12. Briefly, the monoalkylated malonic ester is converted to the sodio derivative and then condensed with either $\text{BrCH}_2\text{CO}_2\text{Et}$ or $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{Et}$ to yield triesters which after saponification, acidification, and decarboxylation give residues containing the respective dicarboxylic acids.

Alcoholic sodium ethoxide solution is prepared by reacting sodium (2.53 g; 0.11 g-atom) with dry alcohol (500 ml). Diethyl ω -(p-chlorophenyl)dodecylmalonate (48.3 g; 0.11 mole) is added dropwise to the stirred mixture at 60°C . During 1 hour ethyl 3-bromopropionate (19.9 g; 0.11 mole) is added to the stirred, refluxing mixture. Refluxing and stirring are continued for 4 hours. To saponify the triethyl 15-(p-chlorophenyl)-1,3,3-pentadecanetricarboxylate formed, 300 ml of 20% aqueous potassium hydroxide solution is added, and the resulting mixture is refluxed 2 hours. After alcohol is flash evaporated from the saponified mixture the alkaline residue is acidified with 6N hydrochloric acid, and the acidified mixture is extracted with ether. Concentration of the ether extract leaves 54 g of crude, syrupy triacid which is decarboxylated by heating for 2 hours at 160°C to yield 45 g of crystalline residue. Principal components of this residue are the desired dicarboxylic acid $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{12}\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ and the monocarboxylic acid $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{13}\text{CO}_2\text{H}$ arising from the saponification and decarboxylation of unreacted diethyl ω -(p-chlorophenyl)dodecylmalonate. The decarboxylated residue is dissolved in a mixture of ether (400 ml) and benzene (400 ml), and the mono- and dicarboxylic acids are coprecipitated as ammonium salts by bubbling an excess of ammonia through the solution. The two ammonium salts are collected by filtration. The mono- and dicarboxylic acids are regenerated by acidification of the ammonium salts, followed by ether extraction and concentration of the ether extract. After being carried through their ammonium salts three times the regenerated mixed acids are resolved by dispersing the mixture in boiling hexane (1000 ml) and allowing it to equilibrate at room temperature. The precipitated dicarboxylic acid is collected and recrystallized again from hexane to yield the analytically pure 2-[ω -(p-chlorophenyl)-dodecyl]glutaric acid (15 g; 32.5% yield). The monocarboxylic acid is precipitated by

cooling the filtrate to -10°C . A recrystallization of this precipitate from toluene leads to the analytically pure ω -(p-chlorophenyl)tetradecanoic acid (10.0 g; 26.8% yield) reported in Table 2. A similar procedure using $\text{BrCH}_2\text{CO}_2\text{Et}$ instead of $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{Et}$ yields the ω -(p-chlorophenyl)dodecylsuccinic acid and ω -(p-chlorophenyl)tetradecanoic acid.

Substituted Silanes: 2-(p-Chlorophenyl)ethyltrichlorosilane,
2-(p-Chlorophenyl)ethyltrimethoxysilane and
2-(p-Chlorophenyl)ethyltriethoxysilane

Steps in the synthesis of $\text{p-ClC}_6\text{H}_4(\text{CH}_2)_2\text{SiCl}_3$ and $\text{p-ClC}_6\text{H}_4(\text{CH}_2)_2\text{Si}(\text{OEt})_3$ are shown in Fig. 5. The chlorophenylethyltrichlorosilane is prepared by condensing vinyltrichlorosilane and chlorobenzene, employing Wagner's variation of the Friedel-Crafts reaction (13). Ethanolysis of the product yields the triethoxy compound. The trimethoxy compound is prepared by reacting 1 mole of the chlorophenylethyltrichlorosilane and 3 moles of methanol in ether using pyridine as a hydrogen chloride acceptor. Properties of the substituted silanes are given in Table 3.

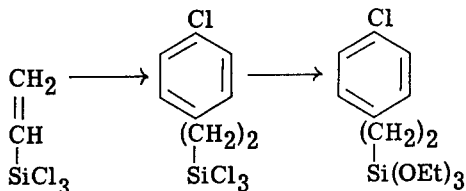


Fig. 5 - Scheme for the synthesis of $\text{p-ClC}_6\text{H}_4(\text{CH}_2)_2\text{SiCl}_3$ and $\text{p-ClC}_6\text{H}_4(\text{CH}_2)_2\text{Si}(\text{OEt})_3$

RESULTS AND DISCUSSION

Conventional criteria such as melting points and elemental assays generally indicate that the reported compounds are of high purity but furnish no information concerning the nature of the impurities. For compounds of such high molecular weights these criteria may not detect significant amounts of homologs, or other compounds containing similar functional groups. In the present study gas-liquid chromatography proved to be an indispensable tool in determining the amounts of such impurities and in assisting in their identification.

Contaminants may arise from impure starting materials, incomplete reactions, and secondary reaction products. A knowledge of these factors serves to limit the list of probable contaminants to a small number. Tentative identifications of some of the contaminants shown as minor peaks in the chromatograms were assigned by matching their retention times (or retention temperatures) with those of probable contaminants. For six of the carboxylic acids of Table 2 the contaminants are known to be carboxylic acids, since the method of purification involves repeated precipitations as the ammonium salts. The tridecanedioic acid observed in the octadecanedioic acid (compound 10 of Table 4) is considered the source of the lower homolog impurity ω -(p-chlorophenyl)octadecyl bromide (compound 6 of Table 4).

Intermediates, carboxylic acids, and silanes bearing the terminal p-chlorophenyl substituent are characterized by conventional criteria in Tables 1, 2, and 3. For further assessment of purity the intermediates and carboxylic acids were analyzed by gas-liquid chromatography. For this analysis methyl esters of the acid compounds were prepared by perchloric acid catalyzed esterification. All analyses were performed on a Beckman GC 4 equipped with a thermal conductivity detector and a temperature programmer. The stainless steel columns, of 1/8-inch OD and 6-ft length, were packed with 3% SE-30 on 60/80 mesh Chromosorb W. Samples were chromatographed under a variety of temperature conditions to obtain a good resolution of the contaminants. Table 4 gives the retention temperatures of the various compounds from a single temperature program, in which the temperature was raised 5.7° per minute from an initial 200°C and helium flow was

Table 4
Results of Gas-Liquid Chromatography of
Intermediates and Carboxylic Acids*

Compound Number	Retention Temperature (°C)	Purity (%)	Probable Impurities and Their Amounts (%)	
			Unchlorinated Analog	Others
1	248	98.9	0	2.9, [†] 3.5 [‡] 4.0 [§]
2	289	96.6	0	
3	235	96.6	1.4	
4	279	97.0	0.8	
5	243	96.4	1.2	
6	286	90.0	1.3	
7	252	83.0	2.0	
8	236	99.6	0.4	
9	249	99.1	0.9	
10	278	96.0	0	
11	290	98.7	0.5	4.0 [§]
12	276	97.4	2.6	
13	282	94.7	1.8	

*Gas-liquid chromatography conditions given in the text.

[†]Compound number 4, $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{18}\text{OH}$.

[‡] $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{13}\text{Br}$.

[§] $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{12}\text{COOH}$.

21 ml per minute. Semiquantitative information concerning the impurities shown in Table 4 was obtained from the chromatograms by the area normalization method. Calculated purities of the six final acid products ranged from 95 to better than 99%.

The typical monocarboxylic acid $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{13}\text{CO}_2\text{H}$ has been analyzed by proton nuclear magnetic resonance. The nuclear magnetic resonance spectra show that the chlorine substitution is more than 95% para and that 1 to 2% of the aromatic rings carry no chlorine substituent (15).

Both mono- and dicarboxylic acids of Table 2 have low melting points ranging from 67 to 88°C. Both types of acids are soluble in common solvents such as ethyl alcohol, benzene, chloroform, and hexane (60°C). The low solubility of the dicarboxylic acids in hexane at 25°C provides a method for separating mixtures containing both types of acids. The three substituted silanes of Table 3 are high boiling liquids requiring storage in evacuated, sealed ampoules to prevent hydrolysis.

Nuclear magnetic resonance studies support the hypothesis that compounds whose syntheses involve both the Wolff-Kishner reduction and the LiAlH_4 reduction contain small amounts of the unchlorinated analogs. Chromatography of these compounds and their derivatives shows an impurity whose retention value is approximately equivalent to that of a homolog of two carbon numbers less than the main compound. It seems reasonable to suppose that this impurity is the suspected unchlorinated analog which would have about the same molecular weight as such a homolog. It is also significant that no such impurity is seen in the keto acid precursors which have not been subjected to reductive procedures.

Principal impurities found in the six p-chlorophenyl-substituted carboxylic acids of this study are homologs and unchlorinated analogs. Such impurities in the amounts found should not interfere in applications for which the compounds were made. Wettability studies on the compounds are reported elsewhere (16).

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